

PATENT SPECIFICATION

(11) 1 213 483

NO DRAWINGS



1 213 483

- (21) Application No. 55322/67 (22) Filed 5 Dec. 1967
 (31) Convention Application No. 600 407 (32) Filed 9 Dec. 1966 in
 (33) United States of America (US)
 45) Complete Specification published 25 Nov. 1970
 (51) International Classification C 07 d 1/14
 (52) Index at acceptance
 C2C B4B B4M
 (72) Inventors DAVID BROWN, JOSEPH PORCELLI JR.
 and EDITH REID FLASTER

(54) PRODUCTION OF ETHYLENE OXIDE

- (71) We, HALCON INTERNATIONAL, INC., of 2 Park Avenue, New York 16, New York, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to the production of ethylene oxide. More particularly, the invention relates to the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene.
- 15 It is well-known that the silver catalyzed oxidation of ethylene to ethylene oxide with molecular oxygen can be controlled by the employment of diluents, such as nitrogen, carbon dioxide, steam and other gaseous materials, inert under the conditions of the reaction, in the reaction zone. However, while some degree of control is thereby maintained over the reaction, and controlled oxidation of ethylene to ethylene oxide may be effected, the conversion of ethylene and the selectivity of the reaction are such that there is room for considerable improvement.
- 20 It is taught in the prior art that the presence of methane in the diluent material may permit the obtention of additional control with the attendant advantage of improved efficiency. However, even this process suffers from the disadvantage of requiring substantially pure ethylene feedstock since the inclusion of other saturated hydrocarbons normally present, such as ethane, is regarded as particularly harmful to the selectivity of the reaction and as exerting a decidedly depressing effect upon ethylene oxide yield. In point of fact, the prior art goes far beyond theoretical conjecture and offers seemingly clear and convincing empirical data to support its position that optimum production rate is achieved in the total absence of
- ethane and that as the ethane content of the total feed to the reactor is increased, the production rate is substantially decreased. It is also taught in the prior art that ethane causes reduced production rates and should be maintained below 1 mol% and preferably below 0.2 mol% of the total feed to the reaction. Accordingly, even in those ethylene oxide processes wherein oxidation is effected with high purity oxygen, i.e., at least about 85 mol%, small quantities of ethane in the ethylene feedstock tend to be detrimental in that the overall yield of ethylene oxide product is thereby substantially reduced. Generally, minimization of ethane in ethylene feed is effected by the installation of auxiliary scrubbing equipment for removal of paraffins from the feed ethylene. The cost of such installation and equipment and the operation thereof impose a significant economic penalty on the manufacturer. Other removal treatments may comprise such unit operations as distillation, absorption, adsorption, extraction, and the like. It has also been suggested that molecular sieves, such as the highly porous adsorbents composed of crystalline sodium and calcium aluminosilicates, after heating to remove water of hydration, be employed to preferentially adsorb ethylene, the adsorbed ethylene being thereafter stripped for recycle by means of an inert gas at elevated temperature. Whatever the technique employed it is apparent that additional equipment and processing operations are required which impair the overall efficiency and economy of the ethylene oxide process.
- 25 The present invention provides an improved process for the production of ethylene oxide in which the foregoing disadvantages of the prior art are reduced or avoided, which allows the use of impure ethylene, and which employs ethane as a reaction gas heat capacity modifier.
- High oxygen concentration may also be

employed in the reaction gas mixture to improve productivity.

In our British Patent Specification No. 1,055,147, there is described and claimed a process for producing ethylene oxide by the partial oxidation of ethylene by means of gaseous oxygen in the presence of a silver containing catalyst, which comprises operating with a concentration of oxygen in the range of 1 to 10%, a concentration of ethylene in the range of 1 to 30%, a concentration of carbon dioxide in the range of 0.1 to 10%, a concentration of halogenated inhibitor in the range of 0.0001 to 100 p.p.m., a concentration of methane and/or ethane in the range of 0.001 to 40%, a reactor temperature in the range of 150° to 400°C., a reactor pressure in the range of 50 to 650 p.s.i.g., a flow rate in the range of 50 to 1500 standard cubic feet per hour per elongated zone with the zone average diameter in the range of 0.5 to 2.0 ins. and the zone length in the range of 5 to 40 ft., the particular combination of conditions being controlled to provide a selectivity in the range of 60% to 80% and an ethylene oxide concentration in the exit gas in the range of 0.3 to 5.0%.

In our British Patent Specification No. 1,075,454, there is described and claimed a process for producing ethylene oxide by the partial oxidation of ethylene by means of gaseous oxygen in the presence of a silver containing catalyst, which comprises operating with three reaction zones in series, with purging from and recycling to each, and each with a concentration of oxygen in the range of 1 to 10% by volume, a concentration of carbon dioxide not in excess of 10% by volume, a concentration of halogenated inhibitor in the range of 0.0001 to 100 p.p.m. by weight, a concentration of methane and/or ethane in the range of 0.001 to 40% by volume, a reactor temperature in the range of 150° to 400°C., a reactor pressure in the range of 50 to 650 p.s.i.g., a flow rate in the range of 50 to 1500 standard cubic feet per hour per elongated zone with zone average diameter in the range of 0.5 to 2.0 ins. and the zone length in the range of 5 to 40 ft., the particular combination of conditions being controlled to provide in the first zone a concentration of ethylene in the range of 7 to 20% by volume, a selectivity in the range of 65 to 75% and a conversion in the range of 10 to 30%, in the second zone a concentration of ethylene in the range of 2 to 5% by volume, a selectivity in the range of 60 to 70% and a conversion in the range of 50 to 25%, and in the third zone a concentration of ethylene in the range of 0.5 to 3% by volume, a selectivity in the range of 60 to 65% and a conversion in the range of 90 to 50%, and an ethylene

oxide concentration in the exit gas in the range of 0.3 to 5.0% by volume.

In the process according to the present invention for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, ethane is provided as a component of the total feed to the reaction in an amount of at least 10 mol% of said feed and a catalyst activity inhibitor (e.g. ethylene dichloride) is employed in an amount of from 5 to 70 parts per million by weight.

The ethane employed in the process may be introduced in the ethylene feedstock, in which ethane is present as an impurity or the ethane may be introduced to the reaction gas from a separate source. Furthermore the ethane may be introduced to the reaction gas partially as an impurity in the ethylene feedstock and partially as an independent feed stream from a separate source. Regardless of how the ethane is introduced to the process, the process is operated in such manner as to achieve a relatively high concentration of ethane in the gas in the reaction zone. As a result of such operation higher productivities may be achieved by permitting the employment of higher oxygen concentrations. Since oxygen exerts a nominal influence on selectivity and reaction rate, improved productivity is obtainable without an attendant penalty. Further, as the ethane serves to moderate the peak reaction temperature, reaction selectivity may also be improved. Employment of ethane in the reaction gas together with the specified amount of catalyst activity inhibitor and optionally with optimum temperature may result in a substantial economic improvement over prior art processes wherein ethane is removed from the feedstock prior to catalytic oxidation of ethylene.

More specifically, the invention comprises a process for the production of ethylene oxide by vapor phase reaction of ethylene and oxygen, wherein the feed to the reaction comprises ethylene, oxygen, at least 10 mol% ethane and from 5 to 70 p.p.m. by weight of catalyst activity inhibitor. Obviously, the concentration of oxygen in the reaction gas mixture must be such as to fall short of the flammable limit; that is, the concentration at which burning or even explosion may occur. This limit may also be regarded as the point where zero selectivity or complete oxidation can occur initially. Ethane permits broader ranges than the prior use of nitrogen, argon, or methane.

In carrying out the invention, components in the total feed to the reaction expressed as mol or volume percent may be:

	Broad	Desirable	Preferred
Ethylene	4-40	6-35	15-30
Oxygen	6-15	8-14	10-13
Ethane	10-80	20-70	40-60

It is generally preferred to employ the catalyst activity inhibitor in the reaction gas mixture in an amount of 10 to 200 ppm (parts per million) by weight.

5 In addition to ethylene dichloride, the preferred inhibitor, other agents capable of exerting an inhibiting effect upon the catalytic oxidation reaction may be utilized. The latter include other halogen-containing
10 compounds, including other chlorinated hydrocarbons, as well as chlorinated polyphenyl compounds. Unlike the prior art teaching, however, the amounts of such compounds which may suitably be used in
15 the process of the present invention are not limited to relatively small quantities, for example less than 10 ppm, but may embrace quantities greater than 10 ppm, for example
20 up to 70 ppm. Also, mixtures of the various inhibitors heretofore employed may be used to advantage in the process of the invention.

In one embodiment of the invention, when starting with a commercial ethylene fraction containing a substantial amount, at least 10
25 mol%, of normally gaseous paraffins having more than one carbon atom, the ethylene in its impure commercial form is fed directly into the reaction zone.

In the production of ethylene oxide by the silver-catalyzed controlled oxidation of
30 ethylene with molecular oxygen in accordance with the invention, the reactants comprising ethylene, oxygen and ethane are passed over a catalyst containing metallic silver at conditions of temperature and pressure
35 resulting in the interaction of ethylene and oxygen with the formation of reaction products comprising ethylene oxide.

Catalysts employed in the process of the
40 invention comprise any of the silver metal-containing catalysts disclosed in the prior art capable of catalyzing the controlled oxidation, with molecular oxygen, of ethylene to
45 ethylene oxide. These comprise the catalysts consisting essentially of silver metal upon a suitable support. Suitable supports comprise, for example, any of the siliceous and aluminous support materials heretofore
50 employed. Particularly suitable catalysts comprise those consisting essentially of silver metal upon such supports as alundum, silicon carbide, silica, carborundum, or any of the many alumina supports. Suitable
55 catalysts comprise, for example, those disclosed and claimed in the U.S. Patents 3,207,700 and 2,752,362. It is to be understood, however, that the present invention is in no way limited to the use of any specific silver metal-containing catalyst.

60 The silver metal catalyst used in the process of the invention may be in the form of a stationary bed, or it may be used in fluidized or suspended form. The process is applicable to the use of a plurality of
65 catalytic oxidation zones, arranged in series

or in parallel. When using a plurality of such zones, reactants and/or added ethane may be introduced into one or more thereof. Conditions within such zones need
70 not be the same, but may be varied and reaction products may be separated, or not, between such zones. Any part, or all, of the reactants, ethane and/or diluent materials may be introduced into one or more
75 of the reaction zones at more than one point thereof.

The controlled oxidation reaction is carried out at temperatures in the range of, for example, from 150 to 450°C., and preferably
80 in the range from 200 to 300°C. Pressures in the range of from atmospheric to 500 p.s.i.a. are generally employed, while a range of from 250 to 350 p.s.i.g. is preferred. Higher pressures, may, however, be used.
85 Diluent materials such as, for example, nitrogen, carbon dioxide and steam may be present in varying amounts. Such diluents may be introduced into the systems wilfully from within the system alone or together
90 with ethane and/or unreacted ethylene taken from the reactor effluent.

Molecular oxygen employed as reactant in the process may be obtained from any suitable source. The suitable oxygen charge
95 may consist essentially of relatively pure oxygen or a concentrated oxygen stream comprising molecular oxygen in major amount with a lesser amount of one or more diluent inert gases such as, for example,
100 nitrogen, argon and the like. A preferred concentrated oxygen gas, suitable for use as the make-up oxygen reactant in the process of the invention, comprises the concentrated oxygen gas consisting essentially
105 of oxygen, nitrogen and argon obtained, for example, from air by suitable separating means comprising one or more such steps as fractionation, low temperature distillation and other conventional separating means.
110 The suitable oxygen-containing gas preferably has an oxygen concentration of at least 85 mol%. Since the amount of gaseous materials which must be vented from the oxidation process varies directly with the
115 increase in inert gaseous diluents introduced, and any increase in materials vented is generally accompanied by a decrease in yield of ethylene oxide from ethylene feed, it is preferred to employ molecular oxygen gas having the higher values for oxygen concentration, for example from 85 to 98 mol%.
120 Particularly preferred is the use of a concentrated oxygen gas containing from 90 to 97 mol% of molecular oxygen. The concentration of oxygen in the total feed to the ethylene zone may vary. Generally the concentration need not exceed 12 mol% of the total reactor feed. As aforementioned, care must be exercised to maintain the oxygen
125 concentration in the charge somewhat below 130

the flammable limit for the specific conditions employed.

The process of the invention may be practised with a relatively broad concentration of ethylene in the total charge to the reaction zone. Thus, ethylene may constitute, for example, broadly from 4 to 40 mol% of the total feed to the ethylene reaction zone. A concentration of ethylene in the total reactor feed of from 6 to 35 mol% is desirable, while 15 to 30 mol% is particularly preferred. Higher or lower ethylene concentrations may however be used. Maintaining a specifically desired ethylene concentration is facilitated by controlled addition of ethane and by control of the amount of materials, such as, for example, methane, nitrogen, carbon dioxide and argon, recycled from within the system.

Unexpectedly, it has been found that contrary to the prior art, it is unnecessary to maintain a critical mol ratio of ethylene to oxygen in excess of 1 in the total feed to the reaction zone. Furthermore, irrespective of ethylene and oxygen relative concentrations, carbon steel reactor tubes may be used, as well as alloy steel tubes.

Thus, the improved efficiency and productivity advantages achieved by the process of the present invention are achieved with even less of the rigorous and complicated controls required by prior art processes.

The ethane used in the process of the invention may be obtained from any suitable source. It should be noted that in contrast to the prior art methane process aforementioned, the presence of paraffinic hydrocarbons other than ethane is not detrimental to the process of the present invention. Suitable sources of ethane comprise, for example, natural gas, normally gaseous by-product streams containing ethane with or without paraffins, obtained in thermal hydrocarbon conversion processes, etc. Where ethane is introduced into the system from an independent source, it may be combined directly with a part or all of the make-up ethylene, the recycle stream or with the feed at the point of entry into the oxidation zone. A part or all of such ethane entering the system may be introduced as a separate stream into the reaction zone along one or more points along the length thereof.

The process of the invention and the improved productivity obtainable thereby are illustrated by the following Examples.

Example 1

This example was conducted for the purpose of providing a standard or reference base where substantially no ethane is contained in the total feed to the ethylene oxidation zone. In this example ethylene was oxidized to ethylene oxide by reacting

ethylene with molecular oxygen in the presence of a supported silver metal catalyst at a temperature of 250°C and a pressure of 315 p.s.i.a. The make-up ethylene charge consisted essentially of 100% ethylene at a flow rate of 1.14 pounds per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen and had a flow rate of 1.66 pounds per hour. An independent fresh nitrogen charge, substantially 100% nitrogen, at a flow rate of 0.01 pounds per hour, completed the make-up charge streams. To the make-up gas streams, recycle gas, at a flow rate of 50.7 pounds per hour, was added. This recycle gas had a molar composition of 15.2% ethylene, 4.6% oxygen, 7.4% carbon dioxide, 32% argon, and 40.8% nitrogen. Resultant total feed to the reactor flowed at a rate of 53.5 pounds per hour, and had a molar composition of 17% ethylene, 7.5% oxygen, 7% carbon dioxide, 30% argon and 38.5% nitrogen. To this feed was added 0.5 ppm by weight of ethylene dichloride. Ethylene oxide was recovered from the reactor effluent by absorption in water followed by distillation of the rich aqueous absorbate. Residual reactor gaseous effluent, free of reaction products comprising ethylene oxide, was returned as the recycle gas to the reaction with the exception of a small constant bleed from the system. Determination of the difference between the outlet and inlet ethylene oxide at the reactor provided a Δ EO value of 1.75. The Δ EO value is commonly employed as a yardstick since it is proportional to ethylene oxide productivity. The overall yield of this example was 68.6%.

Example 2

This example is illustrative of the invention and was conducted with ethane present in the total feed in substantial amount as a ballast. In this example make-up ethylene charge, comprising of essentially 100% ethylene, was employed at a flow rate of 1.31 pounds per hour. The make-up oxygen gas charge comprising essentially 99.5% oxygen, was employed at a flow rate of 1.87 pounds per hour. The third and final charge stream consisted essentially of 100% ethane gas at a flow rate of 0.02 pounds per hour. A recycle gas, at a flow rate of 50.3 pounds per hour was mixed with the make-up streams. The molar composition of the recycle gas comprised 15.2% ethylene, 8.0% oxygen, 7.5% carbon dioxide, 17% argon and 52.3% ethane. Resultant total feed, at a flow rate of 53.5 pounds per hour was introduced to the reactor, which contained the same type catalyst and was maintained at the same temperature and pressure conditions as the reference run. The molar composition of the total feed was 17% ethylene, 11% oxygen, 7% carbon dioxide,

16% argon and 40% ethane. Ethylene dichloride inhibitor in an amount of 15 ppm by weight was added to the reaction gas. The Δ EO value determined for this example was 1.92, while the overall yield was 68.6%.

Example 3

A second example of the process of the invention was carried out with ethane present in the total feed, in substantial amount as ballast, but with an increased ethylene concentration. The make-up ethylene charge in this example consisted essentially of 100% ethylene at a flow rate of 1.45 pounds per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen and had a flow rate of 2.08 pounds per hour. An independent make-up charge of essentially 100% ethane, at a flow rate of 0.2 pounds

per hour was also employed. A recycle gas, at a flow rate of 49.95 pounds per hour was mixed with the make-up charge streams. This recycle gas had a molar composition of 23.6% ethylene, 7.7% oxygen, 7.6% carbon dioxide, 14% argon and 47.1% ethane. The total feed to the reactor, at a flow rate of 53.5 pounds per hour, had a molar composition of 25% ethylene, 11% oxygen, 7% carbon dioxide, 13% argon, and 44% ethane. Ethylene dichloride in an amount of 15 ppm by weight was introduced to the reactor as an inhibitor. The Δ EO value for this example was determined to be 2.13 while the overall yield was 68.6%.

The composition and results of the foregoing reference and invention Examples are set forth, for ease of comparison, in Table I:

TABLE I

						Prior Art	Invention		
						Example 1	Example 2	Example 3	
40	Ethylene	17	17	25	
	Oxygen	7.5	11	11	
	Carbon Dioxide	7	7	7	
	Argon	30	16	13	
	Nitrogen	38.5	—	—	
45	Ethane	—	49	44	
	Ethylene Dichloride	0.5 ppm	15 ppm	15 ppm	
	Δ EO	1.75	1.92	2.13	
	Overall Yield	68.6%	68.6%	68.6%	

NOTE. Components of reaction gas mixture are given in terms of mol or volume percent except ethylene dichloride which is in terms of parts per million by weight.

Examination of the results in Table I indicates that the utilization of ethane as a major component of the total feed provides a significant improvement in productivity of ethylene oxide, of the order of 10%, without any sacrifice in overall yield. This improvement is apparently directly attributable to the increased oxygen concentration in the reaction gas mixture. It will be noted from Example 3 that where inlet reaction conditions are substantially the same, with the sole exception of increased ethylene concentration in the reaction gas mixture, even further improvement in ethylene oxide productivity is obtained, the productivity improvement in Example 3 as compared with Example 1 being of the order of 22%.

Although the invention has been described in connection with certain specific examples, it will be readily apparent to those skilled in the art that various modifications in composition and procedure may be made to suit specific requirements without departing from

the scope of the invention as defined in the annexed claims:

WHAT WE CLAIM IS:—

1. In a process for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, the improvement which comprises having in the oxidation reaction mixture ethane in an amount of at least 10 mol% and a catalyst activity inhibitor in an amount of from 5 to 70 parts per million by weight.

2. A process according to Claim 1 wherein a substantial portion of the ethane is provided in the ethylene feed, the ethane being present in an impurity therein.

3. A process according to Claim 1 wherein the ethane is provided by independent ethane feed.

4. In a process for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, the improvement comprising passing a gas mixture over a silver-containing catalyst in a reaction zone at ethylene oxide forming conditions, said gas mixture com-

- prising ethylene, oxygen, at least 10 mol% ethane, and from 5 to 70 parts per million by weight of a catalyst activity inhibitor.
5. A process according to Claim 4 wherein the gas mixture comprises impure ethylene, said ethylene containing ethane as the major impurity.
6. A process according to Claim 4 wherein the gas mixture comprises essentially ethane-free ethylene and ethane is introduced to the reaction gas from a separate source.
7. A process according to Claim 4 wherein the gas mixture comprises ethane-containing ethylene and ethane from a separate source.
8. A process according to Claim 4 wherein the gas mixture comprises high purity oxygen.
9. A process according to Claim 8 wherein said oxygen has a purity of at least 85 mol%.
10. A process according to any of Claims 1 to 9 wherein said catalyst activity inhibitor is present in an amount effective for the purpose of counteracting any selectivity reduction attributable to the presence of ethane.
11. A process according to any one of Claims 4 to 10 wherein the gas mixture comprises
- | | |
|-----------|--------------------|
| Ethylene | 4—40 mol% |
| Oxygen | 6—15 mol% |
| Ethane | 10—80 mol% |
| Inhibitor | 5—70 ppm by weight |
12. A process according to Claim 11 wherein the gas mixture comprises
- | | |
|-----------|--------------------|
| Ethylene | 6—35 mol% |
| Oxygen | 8—14 mol% |
| Ethane | 20—70 mol% |
| Inhibitor | 5—70 ppm by weight |
13. A process according to Claim 12 wherein the gas mixture comprises
- | | |
|-----------|---------------------|
| Ethylene | 15—30 mol% |
| Oxygen | 10—13 mol% |
| Ethane | 40—60 mol% |
| Inhibitor | 10—20 ppm by weight |
14. A process according to Claim 13 wherein the gas mixture comprises
- | | |
|---------------------|------------------|
| Ethylene | 17 mol% |
| Oxygen | 11 mol% |
| Ethane | 49 mol% |
| Ethylene Dichloride | 15 ppm by weight |
15. A process according to Claim 13 wherein the gas mixture comprises
- | | |
|---------------------|------------------|
| Ethylene | 25 mol% |
| Oxygen | 11 mol% |
| Ethane | 44 mol% |
| Ethylene Dichloride | 15 ppm by weight |
16. A process according to any one of the preceding Claims wherein said gas mixture comprises fresh feed stock and cycle gas.
17. A process according to any one of the preceding Claims wherein said reaction zone is maintained at a temperature in the range of about 150° to about 450°C. and a pressure in the range of about atmospheric to about 500 p.s.i.a.
18. A process according to Claim 17 wherein said reaction zone is maintained at a temperature in the range of about 200° to about 300°C. and a pressure in the range of about 250 to about 350 p.s.i.a.
19. A process for the production of ethylene oxide substantially as hereinbefore described and exemplified by Example 2 or 3.
20. Ethylene oxide when produced by the process of any one of the preceding claims.

MATHYS & SQUIRE,
Chartered Patent Agents,
10, Fleet Street, London, E.C.4.
Agents for the Applicants.